

Enhancing the Growth of Plants on Coal Waste Using a Biological Fertilizer

Peter J. Leggo

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK.

pjl46@cam.ac.uk

Abstract

A biofertilizer, composed of a mixture of crushed zeolitic tuff and organic waste, has been used to grow plants on coal waste. The growth experiment is reported together with control experiments to demonstrate the efficacy of the biofertilizer. Plants used were: *Brassica napus*, *Beta vulgaris*, *Linum usitatissimum* and *Zea mays* which were grown in pots under controlled greenhouse conditions. Coal waste from a Nottinghamshire colliery in the English Midlands was used throughout the work as the plant substrate. Decomposition of the organic waste produces ammonium ions which are adsorbed by the zeolitic tuff, and when the mixture is added to a plant substrate, oxidizing ammonium micro-organisms function and sponsor nitrification (Leggo et al., 2009). The resulting growth enhancement is exceptional as shown by the shoot dry weight of the plants harvested at maturity.

Keywords

Coal Waste; Organic Waste; Decomposition; Ammonium Ions; Zeolitic tuff; Micro-Organisms; Enhanced Growth

Introduction

The use of chemical fertilisers, over the last 60 or more years has been of great benefit in keeping world food crop supply ahead of population growth. However, this achievement has not been without a cost to soil health and the environment. It is commonly found that natural nitrification has been reduced to a very low level in the arable soils of developed countries. Current agricultural practice relies heavily on the annual use of inorganic fertilizers to provide economic crops. It is now known that without a regular input of organic matter (OM) the over use of nitrogen, phosphorus, potassium (NPK) fertilizers causes nutrient limited microbes to rapidly decompose the soil OM which, in turn, can lead to a structure-less soil with less capacity to hold water; causing greater runoff and groundwater pollution, (Ball, 2006). In addition to the high energy costs of the Haber-Bosch process for producing ammonia from atmospheric nitrogen, the source of natural phosphate is becoming less readily available. The organo-zeolitic biofertilizer

appears not to suffer the disadvantages of the conventional NPK fertilizers in being potentially less expensive, particularly in countries that have zeolitic tuff resources, easier to produce in terms of energy costs and of greater benefit to the soil environment. It has been known for several decades that natural zeolites, in the form of volcanoclastic sediment, are of world wide occurrence. Zeolites are unique among the rock forming silicates having porous crystal lattice structures that adsorb water and extraneous cations. The mineral used in this work is clinoptilolite which is a zeolite highly selective to the exchange of ammonium ions, with only caesium, rubidium and potassium having high selectivity. Tuffaceous rocks containing clinoptilolite commonly have a high abundance of this mineral reaching 80-90 volume % in many cases. F.A. Mumpton did much to develop the mineralogy and geological occurrence of natural zeolites and their industrial and agricultural applications (Mumpton 1977). This considerable task was initially given as "Short Course Notes" published by the Mineralogical Society of America under the title "Mineralogy and Geology of Natural Zeolites" edited by F.A. Mumpton, in 1977. Since then, scientific papers, books and conferences have led to a much greater understanding of the properties of natural zeolites and their use. The high selective adsorption capacity of the ammonium ion (NH_4^+) by natural zeolites has long been recognized (Barrer and Gibbons, 1963; Ames, 1967) and the necessity to remove this ion from sewage effluent and wastewater has led to the use of rocks containing common zeolite minerals such as clinoptilolite, mordenite, phillipsite and chabazite (Hagiwara and Uchida, 1978). In earlier work (Mercer, Ames, Touhill, Van Slyke and Dean, 1969) it was discovered that zeolitic tuff, containing an abundance of clinoptilolite, was very effective in the removal of the ammonium ions from secondary effluent and research on the application of natural zeolites to water and wastewater treatment has been the subject of a review (Kalló, 2001). Further, work on the removal of

ammonium ions from municipal wastewater (Semmens, Wang and Booth 1977; Murphy et al., 1978) showed that an increase in nitrate occurred in the treated water which was indicative of the conversion of ammonium to nitrate ions, suggesting that biological activity was responsible. Later, it was shown (Garcia, Gonzales, Notario and Arbelo, 1992b) that this behaviour was associated with nitrifying micro-organisms present in extracellular polymers (biofilm) formed on the zeolitic tuff. This earlier work has led to a working hypothesis, supported by further laboratory studies, which proposes that by composting a mixture of crushed zeolitic tuff and organic waste ammonium ions from the decomposing organic matter are exchanged to the zeolite lattice. When this mixture (the biofertilizer) is added to a plant substrate ammonium oxidizing micro-organisms initiate nitrification. A time-course experiment, lasting 180 days, involving the leaching of a soil amended with the biofertilizer, showed that the concentration of NH_4^+ ions, loosely bound to the zeolite surface, reaches a peak at some 60 days after which they are rapidly lost. (Leggo and Ledésert, 2009b) Coincidental with the loss of the NH_4^+ ions, it was found that the nitrate concentration of the leachates reached a maximum in a similar time. This behaviour, it is thought, demonstrates that nitrifying micro-organisms oxidise the available NH_4^+ ions, produced by the bio-fertilizer, followed by further oxidation to nitrate. After one hundred days, a slight increase occurred in the concentration of NH_4^+ followed by a steady decline to the end of the experiment. Other experimental work, on the microbial diversity of soil containing organic material amended with clinoptilolite, has shown that a number of micro-organisms undergo short as well as long term changes. In the case of nitrifying bacteria, changes in the quantity and biomass over 22 days were seen to have a pulsating nature (Andronikashvili, Urushadze, EpiKashvili, Gamisonia and Nakaidze 2008). In this respect, the use of laboratory bioreactors has shown that in substrates containing organic material, autotrophic nitrifiers in biofilms are slowly replaced by heterotrophic bacteria (Lee et al., 2004). Work on biofilms and extracellular matrices on geomaterials support this observation in as much that colonization of one species by another appears to be the norm (Kemmling et al., 2004).

In experiments to study the characteristics of the pore water, in substrates amended with the biofertilizer, the electrical conductivity was shown to increase by over an order of magnitude relative to the un-treated

substrates, demonstrating the high ionic mobility of these solutions (Leggo and Ledésert 2001). It is found that nitrification is responsible for proton activity, due to the ensuing enzyme reactions and it is thought that the free hydrogen ions produced react with the substrate pore-water to form hydronium ions (H_3O^+) which quickly re-equilibrate and remove cations from the substrate (Preston and Alleman 1993; Süsser and Schwertmann 1991). The released cations cover a large range of elements that then become available for plant uptake. Chemical analysis of plant leaf tissues has demonstrated that the concentration of major nutritional elements together with essential and beneficial trace elements is taken up by plants growing in the amended substrates contrast with those from plants grown in un-treated substrates. The fact that the plants grown in the amended substrate exhibit such a high degree of growth enhancement and superior quality, has led to the conclusion that the greatly increased ionic mobilization of the pore water allows ion-homeostasis to control the uptake behaviour of the plant (Leggo, et al., 2010).

Materials and Methods

The amount of crushed zeolitic rock used in an amended substrate is in the order of 8-9 volume percent which is represented by 70 kg of rock per tonne of treated substrate; affordable where transport costs are low. The biofertilizer is made from a mixture of organic waste and crushed clinoptilite tuff, with a particle size of 0.5 – 2.0 mm. These materials are mixed in a ratio of two parts organic waste to one part zeolitic tuff by volume. During composting the mixture soon loses its malodour and becomes easy and safe to handle. The resulting biofertilizer is then added to a substrate in a ratio of one part to five by volume.

In this work, the plant substrate was coal waste taken from a former colliery near Nottingham, in the English Midlands. The colliery is situated some 14 Km NNE of the city of Nottingham in an area that was formally part of Sherwood Forest. The site was a working coal mine until 1999 after which production ceased and the underground workings were closed and the site cleared of buildings. The coal waste present on the site was levelled and covered with a layer of sand and soil. Grass seed was sown on the levelled ground. The growth of grass is limited by the thickness and nutrient content of the sand/soil overburden and in many places rainfall has eroded the surface producing

areas which expose the underlying coal waste. The waste used in the experiments was taken from an area where the soil overburden had been washed away and can be described mostly as being coal fragments mixed with shale and a small amount of assorted stony rubble. As it was not possible to avoid plant predation by wild animals a 50 kg sample of the coal waste was taken and used for pot experiments conducted in a laboratory greenhouse at the University of Cambridge Botanic Garden. An homogenised sample of the coal waste was taken for chemical analyses to measure the concentration of 25 elements, Table 1. The average density of the waste was found to be $0.75 \pm 0.04 \text{ g.cm}^{-3}$ and to have a pore-water pH of 4.9 ± 0.1 . It was thought necessary to add lime to increase the porewater to a pH of 6.5; which was achieved by the addition of 5 g of CaCO_3 / kg of substrate.

The zeolitic tuff used in this work has a clinoptilolite abundance of some 80 volume per cent with mixed clays, cristobalite, quartz and pyroclastic minerals making up the total. In this respect, it is a typical zeolitized volcanoclastic rock having an original magma chemistry characteristic of rhyolite to andesite composition; that is, a high to intermediate silica content (65 - >70 weight percent silica). Poultry manure was used as the organic component and when mixed with the crushed zeolitic tuff and composted, an odourless, dry and friable biofertilizer is produced, which is freely dispersed when mixed with soil. The powdered activated carbon, used as substrate number(2) of the extended control experiment, was obtained from the Sigma-Aldrich Company; designated product number C.5385.

The plant species used were; *Brassica napus* (Oil Seed Rape), *Linum usitatissimum* (Linseed), *Beta vulgaris* (Sugar Beet) and *Zea mays* (Sweet Corn). For the purpose of the growth experiments, these were sown initially into five substrates, shown in Table 2. Garden soil coming from the Cambridge University Botanic Garden has been described in earlier work (Leggo, 2000). The mass of the substrates, depending on the size of the plant, varied from one to three kilogram as shown in Table 2. Apart from the case of *Z. mays*, in which only one plant was grown per pot, two plants per pot were grown to maturity. The plants were watered regularly and sodium light was used, during the winter months, to extend the daylight hours. The coal waste amended with the biofertilizer was treated with lime (CaCO_3) to increase the pH of the substrate porewater from a value of 4.9–5.0 to approximately 6.0.

This was thought to be necessary to maintain the function of the nitrifying micro-organisms that are known to be sponsored by the biofertilizer, (Leggo and Ledésert 2009b).

Substrates used as initial controls were: Garden Soil, Coal Waste, Coal Waste + Zeolitic Tuff and Coal Waste + Lime. Later, after the plants had reached maturity, it was decided to conduct another experiment to extend the number and diversity of the controls, see Table.3. This work was carried out using *B.napus* and in cases where the composition of the amendment varied in as much that one or other of the components of the biofertilizer was replaced by coal waste or garden soil the replaced component was of equal volume. The plants were grown to maturity and the aerial parts removed by cutting the stems one centimetre above soil level. The stems and leaves, seed, corn ears and beet tubers, were bagged and dried to constant weight at 70°C . In the case of the extended control experiment, the plants were harvested 160 days after germination, leaves and stems were removed, dried and weighed as before. In all cases, the dry weights were used to compare the growth of plants in the various substrates.

TABLE 1. CHEMICAL ANALYSIS OF COAL WASTE FROM CALVERTON COLLIERY, NOTTINGHAMSHIRE, UK

Element (mg/kg) \pm S.E. (n = 6)				
B	Na	Mg	Al	Si
42.8 ± 2.1	555 ± 11	2553 ± 202	26838 ± 1962	50682 ± 3842
P	S	K	Ca	Ti
193 ± 46	1758 ± 634	6462 ± 528	5740 ± 627	1034 ± 74
Cr	Mn	Fe	Co	Ni
31.3 ± 3.0	306 ± 26	11139 ± 983	9.46 ± 0.80	32.5 ± 2.6
Cu	Zn	As	Se	Rb
37.5 ± 3.2	24 ± 2.5	17.2 ± 1.6	<2.0	34.8 ± 2.8
Mo	Cd	Cs	Ba	Pb
3.2 ± 0.31	0.16 ± 0.02	2.38 ± 0.21	147 ± 13	22.45 ± 2.0

Coal waste analyses were made by the analytical geochemistry laboratory of the British Geological Survey. After checking for size suitability, 0.25 g of sub-sample was weighed into a PFA beaker and pre-digested over-night with HNO_3 because of the significant organic content of the waste. The samples subsequently underwent a mixed acid digest using concentrated $\text{HF}/\text{HNO}_3/\text{HClO}_4$ and were taken to dryness. The digested material was then re-dissolved in dilute HCl and HNO_3 . Samples were stored in

plastic Nalgene bottles prior to analysis. Three replicate digests were produced and two replicate analyses on each digest were performed. Sample analysis was performed on a Spectro Arcos ICP-AES. Data should be considered accurate to no more than three significant figures. Standard deviations are quoted (n=6).

Results and Discussion

A very large growth enhancement occurred in plants grown in substrates amended with the biofertilizer. In this respect, coal waste is no different from other substrates used in earlier work i.e acidic base metal waste and metal refinery waste, when amended with the biofertilizer, (Leggo et al 2010; Leggo and Ledésert 2009a). The plants were harvested at maturity and the leaves, stems and seeds were dried and weighed as already mentioned. Table 2 shows that the shoot dry weights of plants grown in the coal waste amended with the biofertilizer are far greater than those grown without the amendment. This very large difference is also expressed in the dry weight of the seed collected.

TABLE 2. PLANT DRY WEIGHTS : LEAVES AND STEMS, OIL SEED, CORN. EARS AND BEET TUBERS.

Substrate	Average Plant Wt (g)	Average Seed /Tuber (g)
<i>Zea mays</i> 3 kg substrates, 1 plant per pot, triplicate samples.		
Coal Waste + Biofertilizer + Lime	167.90 ± 5.80	111.93 ± 2.10
Garden Soil	10.74 ± 1.92	0.193 ± 0.03
Coal Waste	5.04 ± 0.26	0.09 ± 0.03
Coal Waste + Zeolitic Tuff	3.19 ± 0.52	0.06 ± 0.02
Coal Waste+ Lime	4.19 ± 0.35	0.06 ± 0.01
<i>Brassica napus</i> 2 kg substrates, 2 plants per pot, triplicate samples..		
Coal Waste + Biofertilizer	37.56 ± 3.87	14.50 ± 3.48
Garden Soil	4.78 ± 2.34	0.91 ± 0.16
Coal Waste	0.93 ± 0.09	0.17 ± 0.03
Coal Waste + Zeolitic Tuff	0.92 ± 0.73	0.05 ± 0.03
Coal Waste + Lime	0.14 ± 0.04	No Seed Recovered
<i>Linum usitatissimum</i> 1 kg substrates, 2 plants per pot, triplicate samples.		
Coal Waste + Biofertilizer	14.06 ± 0.93	2.86 ± 1.15
Garden Soil	1.47 ± 0.26	0.31 ± 0.06
Coal Waste	0.62 ± 0.12	0.17 ± 0.04
Coal Waste + Zeolitic Tuff	0.39 ± 0.09	0.08 ± 0.01
Coal Waste + Lime	0.49 ± 0.04	0.09 ± 0.02
<i>Beta vulgaris</i> 2 kg substrates, 2 plants per pot, triplicate samples.		
Coal Waste + Biofertilizer	110.95 ± 7.98	95.06 ± 5.78
Garden Soil	5.76 ± 1.22	4.01 ± 0.94
Coal Waste	2.18 ± 0.47	1.15 ± 0.28
Coal Waste + Zeolitic Tuff	0.81 ± 0.24	0.38 ± 0.13
Coal waste + Lime	1.72 ± 0.81	0.72 ± 0.71

TABLE 3. EXTENDED CONTROL EXPERIMENT USING B.NAPUS. DRY

WEIGHTS. LEAVES AND STEMS.

Substrate	Average Plant Wt (g)
<i>Brassica napus</i> 2 kg substrates, 2 plants per pot, triplicate samples	
1. Coal Waste + Biofertilizer + Lime	52.92 ± 5.39
2. Coal Waste + Garden Soil + Poultry Manure + Activated Charcoal	50.58 ± 8.02
3. Coal Waste + Biofertilizer - Lime	49.83 ± 7.29
4. Coal Waste + Poultry Manure	31.01 ± 3.50
5. Garden Soil	28.52 ± 3.77
6. Coal Waste + Zeolitic Tuff	24.16 ± 1.92
7. Garden Soil + Poultry Manure	23.59 ± 3.94
8. Coal Waste + Garden Soil + Zeolitic Tuff	9.16 ± 0.58
9. Coal Waste	2.86 ± 0.31

At harvest *Zea mays* grown in amended coal waste had ears, of average weight 167.9 ± 5.8 g whereas those from plants grown in un-amended coal waste had an average weight of 5.04 ± 0.26 g, see Figure 1. A dramatic difference is also observed in the case of *Beta vulgaris*, see Figure 2. Large differences were also found in the seed weight of *Brassica napus* and *Linum usitatissimum* which again demonstrates the growth enhancement of plants cultivated in the biofertilizer amended coal waste, see Table 2.



FIG.1 ZEA MAYS EARS AT MATURITY. THREE REPLICATE EARS FROM PLANTS GROWN IN COAL WASTE SHOWN ABOVE THOSE GROWN IN COAL WASTE AMENDED WITH THE BIOFERTILIZER.

In the separate extended control experiment, a prime requirement was to compare the behaviour of plants grown in soil/manure and coal slag/ manure substrate with those grown in the bio-fertilizer amended

substrates in order to quantify the effect of the manure component. It was also desirable to investigate the effect of the zeolite component without the organic material and to observe the difference made by adjusting the pore water pH to a value of close to 6. Again, it was thought that the substitution of the zeolitic tuff with an alternative micro-porous material that adsorbs ammonium ions would be of considerable interest. Activated carbon was chosen for this purpose. The plants were germinated within a few days and grown for a period of 160 days in greenhouse conditions identical to those of the earlier experiment. The shoot dry weights of these plants are given in Table 3 and the contrast of the effects of the different substrates is shown as a histogram in Figure 3.



FIG.2 *B.VULGARIS* TUBERS AT MATURITY. THREE REPLICATE TUBERS FROM PLANTS GROWN IN COAL WASTE SHOWN BELOW THOSE GROWN IN AMENDED COAL WASTE.

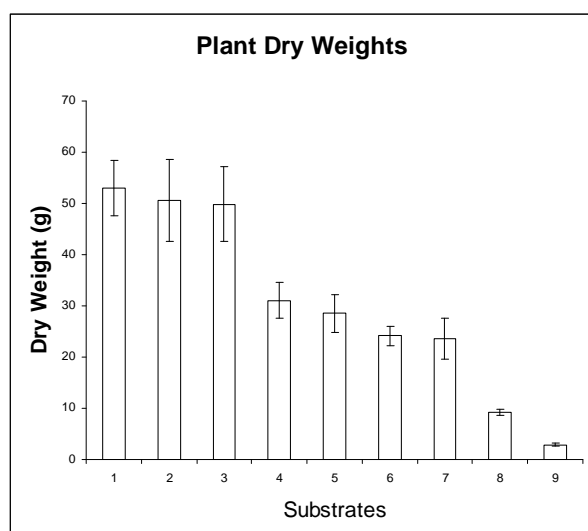


FIG.3 EXTENDED CONTROL EXPERIMENTS USING *B.NAPUS*.; AVERAGE DRY WEIGHT (G), 2KG SUBSTRATES 2 PLANTS PER POT, TRIPLICATE SAMPLES

(1) Coal Waste + Biofertilizer + Lime. (2) Coal Waste +

Garden Soil + Poultry Manure + Activated Charcoal. (3) Coal Waste + Biofertilizer – Lime. (4). Coal Waste + Poultry Manure. (5) Garden Soil. (6) Coal Waste + Zeolitic Tuff. (7) Garden Spoil + Poultry Manure. (8) Coal Waste + Garden Soil + Zeolitic Tuff. (9) Coal Waste.

The concentration of 25 elements present in the coal waste is given in Table 1. According to the well established average concentrations of mineral nutrients in plant shoot biomass that are sufficient for adequate growth (Marschner 1995), it is clear that the wastes contain adequate amounts of the major plant nutrients K and P provided there is a sufficient degree of ionization of the coal waste substrate. This also applies to the minor and trace elements. It has been shown that nitrate levels in aqueous leachates from amended substrates are very high when compared to those from un-amended substrates and it is apparent that the available N is sufficient to sustain the enhanced growth, which is so prevalent in plants grown in the biofertilizer amended substrates (Leggo and Ledésert 2009b).

From this work it appears that coal waste like other industrial waste, for example sulphide mine waste contains chemical elements that can be ionized by the biological activity of the biofertilizer. In this respect plant nutrients which are both essential and beneficial to growth are made available for uptake; as demonstrated by the large differences in biomass between plants grown in the amended and un-amended waste.

The result of the extended control experiment, Figure 3, sheds light on some important features. *B.napus* in substrates with and without the addition of lime, substrates (1) and (3) show little difference in shoot dry weight. As the pH of the coal porewater is known to be very close to 4.0, it is unlikely that the ammonium oxidizing bacteria (AOB) would function well without the addition of lime to raise the pH of the substrate above 6.0. It is suggested, in the light of our current research, that the substrate without the lime addition (3) ammonium oxidizing archaea (AOA), some of which have been found to function at a pH of 4.5, (Gubry-Rangin et al., 2010) might maintain the level of nitrification. The plants grown in substrate (2) in which activated carbon is substituted for zeolitic tuff show no difference in dry weight, within experimental error, with those grown in substrates (1) and (3). Powdered activated carbon is a microporous material that is known to adsorb ammonium ions and

much work has been done on this complex subject (Bandosz and Petit 2009). It appears from our results that the adsorptive properties of this material can simulate those of the zeolitic tuff but more work is needed before this can be better understood. The plants grown in the garden soil substrate (5) have a much greater dry weight than those grown in the coal waste (9) but far below those grown in the coal waste amended with the biofertilizer or activated charcoal. It was also seen that the dry weight of plants grown in the coal waste amended with an equivalent volume of poultry manure (No 4) was little different to that of plants grown in the garden soil substrate (5). It was also found that the dry weight of plants grown in coal waste amended with zeolitic tuff (6) is less than that of plants grown in coal waste amended with poultry manure (4). However, both substrates provide far less nutrient than those amended with the biofertilizer, as observed by the large difference of biomass between those with and without the biofertilizer; thus the organic and zeolitic tuff components are both required to produce the enhancement effect. Insignificant difference, within experimental error, was found between plants grown in substrates numbered (6 & 7) which was not surprising as neither substrate had both components present together in their respective substrates. However, it was surprising that the un-amended garden soil (5) appears to be relatively rich in plant nutrients but as this soil has subsequently been treated with chemical fertilizer it is thought that it contains a residue of such chemicals. Substrate No.8 was composed of coal slag amended with garden soil and zeolitic tuff. This amendment was made to simulate the biofertilizer without the organic component, which, as in the case of substrates 6 and 7, was found not to produce the high degree of growth enhancement seen as a result of using the biofertilizer. Many studies have been made on the selectivity of natural zeolite for various mono and divalent cations. The following series,

$Cs > Rb > K > NH_4^+ > Pb > Ag > Ba > Na > Sr > Ca > Li > Cd > Cu > Zn$
for clinoptilolite shows that NH_4^+ is a relatively highly selective ion (Chelishchev et al., 1992). The analysis of the coal waste (Table.1) shows that both Cs and Rb are regarded as trace element with low concentrations and would not be expected to have a major effect on the uptake of the NH_4^+ ions; whereas K, abundant in poultry manure having a concentration of the order of 1 wt% in the dry condition, would be expected to replace this ion. It is known that NH_4^+ ions are adsorbed by clinoptilolite on preparation of the

biofertilizer, however, in a wet or moist substrate, the transfer of NH_4^+ ions would be expected to undergo slow release during ion-exchange by K^+ (Ming and Allen 2001).

A study of composting, in the present context, has yet to be made but it would appear from work done with sewage sludge that the bulk of ammonia emitted occurs in the first week of composting using a forced air system (Witter and Lopez-Real 1988). This supports the present work in that the transport of NH_4^+ ions was found to occur over a relatively short period. In this respect, it would appear that the biofertilizer, soon after preparation, could be added to a plant substrate as then the transfer of NH_4^+ ions would take place in situ, without a prolonged composting period.

Conclusions

This study has shown that in using an organo-zeolitic biofertilizer plants used as bio-fuels, can be grown and sustained on coal waste. On reaching maturity, these plants show a greatly enhanced growth relative to those grown on un-amended coal waste. By comparing the dry weights of the plants grown in the extended control experiment, it is found that using organic waste without the zeolite component results in 45% of that of plants grown in the amended substrates. A similar result was found when substrates containing zeolitic tuff and no organic waste were investigated. In this instance, the plants had an average dry weights of some 46% of those in substrates amended with the biofertilizer. It was therefore found that the presence of both components of the biofertilizer is essential for it to sponsor nitrification to a degree that produces considerable plant enhancement. As hypothesised, the microbio-logical activity in the amended substrates promotes nitrification whilst supplying hydrogen ions which protonate the pore water, which in turn dissociates cations from the substrate. A plant grown in such an environment then has a free choice of cations, controlled by ion-homeostasis, which produces a healthy plant.

The fact that activated carbon, when used to replace natural zeolite, had a similar effect on stimulating growth focuses attention on the effect of surface absorption in soil amendments. Considering the fact that activated carbon has a high porosity which results in a very large surface area that can absorb NH_4^+ ions, it is not surprising that this material can behave similarly to natural zeolite. Considering other materials such as pillared clays and layered double

hydroxides which possess similar surface charge properties, it might be expected that these would behave in similar fashion. In contrast to conventional inorganic plant fertilizers, the use of which is determined by man, the organo-zeolitic biofertilizer, by virtue of its biogeochemical properties, offers a new approach to plant nutrition. Thus it would appear that considerable scope exists for the use of micro-porous materials that loosely bind ammonia that can be released by ion-exchange and it is expected that continued work will further their agricultural use.

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